

DESCRIPTION

METHOD FOR PRODUCING TETRAFLUOROSILANE

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This is an application filed pursuant to 35 U.S.C. Section 111(a) with claiming the benefit of U.S. provisional application Serial No. 60/508,876 filed October 7, 2003 under the provision of 35 U.S.C. 111(b), pursuant to 35 U.S.C. Section 119(e) (1).

10

TECHNICAL FIELD

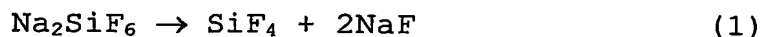
The present invention relates to a method for producing tetrafluorosilane and to use of the compound.

15 BACKGROUND ART

High-purity tetrafluorosilane (SiF_4) is demanded, for example, for materials for optical fibers, semiconductors and solar cells.

As production method for SiF_4 , various methods are known.

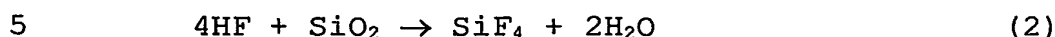
20 Examples of conventionally known methods include a method where hexafluorosilicate is thermally decomposed.



25 However, metal silicofluoride such as hexafluorosilicate contains H_2O and though in a very small amount, an oxygen-containing silicate compound (e.g., SiO_2) as impurities. Therefore, when the compound without being sufficiently pretreated is subjected to thermal decomposition, hexafluorodisiloxane ($(\text{SiF}_3)_2\text{O}$) is generated through reaction between the impurities and SiF_4 (see formula (3) mentioned

below).

Another known method of producing SiF_4 is a method where SiF_4 is produced by reacting SiO_2 with HF in the presence of concentrated sulfuric acid (see JP-A-57-135711).

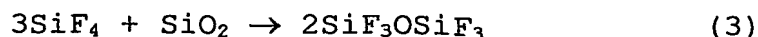


However, this method is problematic in that, when the reaction molar ratio of SiO_2 and HF in the method approaches the theoretical molar ratio, SiF_4 produced may react with SiO_2 to give hexafluorodisiloxane $(\text{SiF}_3)_2\text{O}$.

10 Still another method of producing SiF_4 known in the art is a method where an aqueous solution of hexafluorosilicic acid (H_2SiF_6) is dehydrated and decomposed with concentrated sulfuric acid to produce SiF_4 (see JP-A-9-183608). However, this method also gives hydrogen fluoride (HF) as a by-product like in the
15 above-mentioned thermal decomposition. In the method disclosed, the starting compound H_2SiF_6 is taken out as a side product in a process of producing phosphoric acid, and the by-product HF is brought back to the phosphoric acid production process. Accordingly, since the method indispensably requires
20 the phosphoric acid production process as prerequisite, it is difficult to apply the method to various starting materials.

Still another method of producing SiF_4 also known in the art is a method where H_2SiF_6 is fed into a vertical column reactor and decomposed with sulfuric acid to produce SiF_4 (see JP-A-
25 60-11217 (European Patent No.129112)). Like in the above method, this method also gives hydrogen fluoride (HF) as a by-product and is therefore problematic in that HF is recovered as being contained in sulfuric acid. A method of suspending SiO_2 in H_2SiF_6 and reacting it with HF is described in the document,
30 but this is also problematic in that, when the amount of SiO_2 equimolar to that of HF is fed into the system, $(\text{SiF}_3)_2\text{O}$ is

generated as a side product.



In a case where SiF_4 contains impurity gases such as $(\text{SiF}_3)_2\text{O}$, CO_2 and O_2 , when SiF_4 is used as a starting material for silicon thin films, the impurities may cause contamination with oxygen to adversely affect the characteristics of semiconductors and fibers. Accordingly, a demand for high-purity SiF_4 containing impurities in a smaller amount is increasing.

As a method for purifying SiF_4 that contains $(\text{SiF}_3)_2\text{O}$, CO_2 or HF , for example, there is known a method of treating SiF_4 containing $(\text{SiF}_3)_2\text{O}$ with an adsorbent (see JP-A-57-156317). However, when thus used adsorbent is heated and regenerated, in some cases, its original adsorbability cannot be restored. Although the reason is unclear, it may be assumed that $(\text{SiF}_3)_2\text{O}$ adsorbed by it is decomposed inside the pores of the adsorbent. SiO_2 produced through the decomposition clogs the pores of the adsorbent, and makes it difficult to recycle the adsorbent, causing a problem that the used adsorbent must be discarded as a waste. In addition, if the adsorbent is insufficiently baked before gas circulation, the side reaction with water may cause formation of $(\text{SiF}_3)_2\text{O}$.

DISCLOSURE OF THE INVENTION

The present invention has been made in consideration of the background as above, and its objects are to provide a method for producing tetrafluorosilane from a starting material hexafluorosilicic acid, in which problematic impurities (especially hexafluorodisiloxane) generated in conventional thermal decomposition or sulfuric acid decomposition are efficiently reduced, thereby solving the problem of the side

product HF to give high-purity tetrafluorosilane, and to provide use of the compound.

The present inventors have made intensive studies so as to solve the above problems, and, as a result, have found that

5 SiF_4 can be produced in a process which comprises

step (1) of decomposing H_2SiF_6 with sulfuric acid to give SiF_4 ,

step (2) of reacting HF which has been dissolved in sulfuric acid in step (1) with SiO_2 to give SiF_4 , and

10 step (3) of bringing SiF_4 containing $(\text{SiF}_3)_2\text{O}$ which has been formed in step (2) back to step (1) so that $(\text{SiF}_3)_2\text{O}$ is reacted with HF to give SiF_4 and water, and have also found that, by further subjecting SiF_4 thus produced to a step of contacting it with concentrated sulfuric acid and with molecular

15 sieving carbon, SiF_4 having a much higher purity can be obtained. Based on these findings, the present invention has been completed.

Specifically, the invention relates to a method for producing SiF_4 of the following [1] to [14], and to use of the

20 compound.

[1] A method for producing tetrafluorosilane by decomposing hexafluorosilicic acid with sulfuric acid, which comprises:

a step of decomposing hexafluorosilicic acid in

25 concentrated sulfuric acid in a first reactor to give tetrafluorosilane and hydrogen fluoride, and taking out the thus-formed tetrafluorosilane (step 1);

a step of transferring at least a part of the concentrated sulfuric acid solution of step 1 containing hydrogen fluoride

30 into a second reactor to allow the hydrogen fluoride to react with silicon dioxide which is fed into the second reactor,

thereby producing tetrafluorosilane containing hexafluorodisiloxane (step 2); and

a step of bringing the reaction product of step 2 containing hexafluorodisiloxane and tetrafluorosilane to the first reactor so that the hexafluorodisiloxane in the reaction product is reacted with hydrogen fluoride to convert it into tetrafluorosilane, and taking out the resulting tetrafluorosilane along with the tetrafluorosilane formed in step 1 (step 3).

[2] The method for producing tetrafluorosilane as described in [1], wherein an aqueous hexafluorosilicic acid solution and concentrated sulfuric acid are fed into the first reactor, silicon dioxide is fed into the second reactor each continuously or intermittently, and tetrafluorosilane is continuously or intermittently taken out of the first reactor.

[3] The method for producing tetrafluorosilane as described in [1] or [2], wherein the sulfuric acid concentrations in the first and second reactors are kept 70 mass% or more.

[4] The method for producing tetrafluorosilane as described in any one of [1] to [3], wherein the reaction temperatures in the first and second reactors are 60°C or higher.

[5] The method for producing tetrafluorosilane as described in [1] or [2], wherein the particle size of silicon dioxide fed to the second reactor is 30 μm or less.

[6] The method for producing tetrafluorosilane as described in [1] or [2], comprising a step of contacting the tetrafluorosilane taken out of the first reactor with concentrated sulfuric acid at 50°C or lower so that hydrogen fluoride contained in the tetrafluorosilane is absorbed and removed.

[7] The method for producing tetrafluorosilane as

described in [6], wherein the tetrafluorosilane taken out of the first reactor is countercurrently contacted with concentrated sulfuric acid that is supplied through a channel to the first reactor.

5 [8] The method for producing tetrafluorosilane as described in [1] or [2], comprising a step of purifying the tetrafluorosilane taken out of the first reactor with molecular sieving carbon so as to remove the impurities from the tetrafluorosilane.

10 [9] The method for producing tetrafluorosilane as described in [8], wherein the removed impurities include one or more members selected from the group consisting of hydrogen fluoride, hydrogen chloride, sulfur dioxide, hydrogen sulfide and carbon dioxide.

15 [10] The method for producing tetrafluorosilane as described in [8] or [9], wherein the molecular sieving carbon to be used has a smaller pore size than the molecular size of tetrafluorosilane.

20 [11] The method for producing tetrafluorosilane as described in [10], wherein the molecular sieving carbon pretreated by baking in an inert gas atmosphere and then introducing thereinto high-purity tetrafluorosilane is used.

25 [12] Gas for production of optical fibers, which contains the tetrafluorosilane gas obtained according to the production method as described in any one of [1] to [11], comprising transition metal, phosphorus and boron each at concentration of 100 ppb or less.

30 [13] Gas for production of semiconductors, which contains the tetrafluorosilane gas obtained according to the production method as described in any one of [1] to [11],

comprising transition metal, phosphorus and boron each at concentration of 100 ppb or less.

[14] Gas for production of solar cells, which contains the tetrafluorosilane gas obtained according to the production method as described in any one of [1] to [11], comprising transition metal, phosphorus and boron each at concentration of 100 ppb or less.

DETAILED DESCRIPTION OF INVENTION

The invention is hereinafter described in detail.

The method for producing SiF_4 of the invention substantially comprises

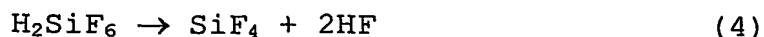
step (1) of decomposing H_2SiF_6 with sulfuric acid to give SiF_4 in the first reactor,

step (2) of introducing at least part of the sulfuric acid of step (1) into the second reactor to cause reaction between hydrogen fluoride dissolved in the sulfuric acid of step 1 and SiO_2 to give SiF_4 , and

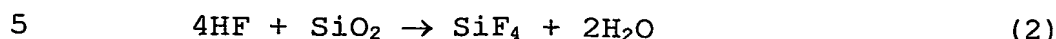
step (3) of bringing SiF_4 containing $(\text{SiF}_3)_2\text{O}$ which has been formed in step (2) back to the first reactor of step (1) so that $(\text{SiF}_3)_2\text{O}$ is reacted with hydrogen fluoride which is a by-product derived from H_2SiF_6 to give SiF_4 . Specifically, as shown in Fig. 1, H_2SiF_6 is decomposed with sulfuric acid in the first reactor (step 1); at least a part of sulfuric acid containing HF as a side product is transferred into the second reactor to react with SiO_2 therein to give SiF_4 containing $(\text{SiF}_3)_2\text{O}$ as an impurity (step 2); and SiF_4 thus formed in the second reactor is brought back to the first reactor so that the impurity $(\text{SiF}_3)_2\text{O}$ is reacted with HF present in the reactor to convert it into SiF_4 (step 3). Through the process, high-purity SiF_4 is collected, and optionally it is further subjected to

purification treatment (purification step).

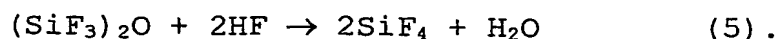
In the process, most of the HF formed in the step 1:



is consumed in the step 2:



and in the step 3:

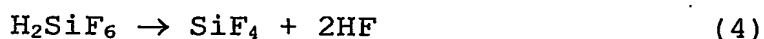


Therefore, the process is free from the problem of HF treatment. In addition, since the side product in step 2,
10 $(\text{SiF}_3)_2\text{O}$ is converted into SiF_4 in step 3, the process is efficient as a whole to give high-purity SiF_4 .

The steps are described individually hereinbelow.

Any H_2SiF_6 produced in any method may be used without any difficulty. For example, H_2SiF_6 produced through reaction of
15 SiO_2 with HF, and H_2SiF_6 produced through reaction of SiF_4 and HF may be used. For example, H_2SiF_6 formed as a side product in a large quantity when Si and F components contained in starting material rock phosphate are decomposed with H_2SO_4 in a process of producing phosphoric acid, which is inexpensive, may be
20 employed in the invention.

The reaction of the step 1 is as follows:

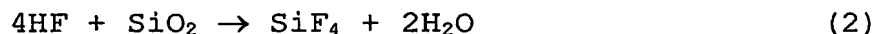


In this step, sulfuric acid serves as a (dehydrating) decomposing agent. However, if the sulfuric acid concentration
25 is low, it is unfavorable since H_2SiF_6 may stably exist in sulfuric acid and is not decomposed. Accordingly, it is preferable that the sulfuric acid concentration after mixed in the reaction system be 70 mass% or more, more preferably 75 mass% or more, most preferably 80 mass% or more. If the reaction temperature
30 is low, it is impractical since the decomposition reaction rate becomes very low. Preferably, the decomposition is performed

at 60°C or higher so as to efficiently obtain SiF₄. However, when the reaction temperature is excessively elevated, it is unfavorable since the proportion of the decomposed side product HF and water in sulfuric acid which evaporate from the aqueous sulfuric acid solution excessively increases while the decomposition reaction may be promoted. Accordingly, the reaction temperature is preferably within a range of 60 to 120°C, more preferably 80 to 100°C.

The shape of the first reactor is not particularly limited as long as it ensures enough time for contact between concentrated sulfuric acid and H₂SiF₆ required for decomposition of H₂SiF₆. Since the decomposition reaction is extremely rapid and may finish in an instant, the contact time within a range of 0.1 to 10 seconds or so is sufficient.

By transferring HF which is formed along with the formation of SiF₄ in step 1, dissolved in sulfuric acid, to the second reactor to react with SiO₂, SiF₄ is prepared (step 2).



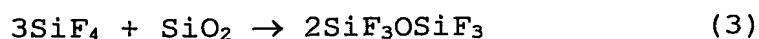
SiO₂ may be solid when subjected to the reaction, but is preferably powdery in order to well disperse in the solution and efficiently undergo the reaction. The SiO₂ powder may be directly fed into the reactor, but its dispersion in sulfuric acid is preferred for continuous addition thereof. The smaller the mean particle size of SiO₂, the better the SiO₂ is dispersed. Preferably, the particle size is preferably 30 μm or less, more preferably 10 μm or less, most preferably 5 μm or less.

The concentration of SiO₂ to be dispersed in sulfuric acid may be suitably determined depending on the physical properties (e.g., particle size, density) of the powder used. However, if the concentration is too low, then the amount of sulfuric acid to be fed to the system may increase; but if too

high, then the slurry may result in solid-liquid separation. Therefore, the SiO₂ concentration preferably falls within a range of 0.1 to 30 mass%. Also preferably, the purity of SiO₂ to be used herein is 90 % or more, more preferably 99 % or more.

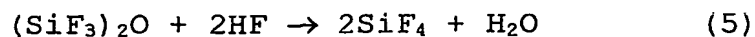
5 The reaction temperature is preferably 60°C or higher, more preferably falling within a range of 80 to 100°C. The amount of SiO₂ to be added to the system may be a theoretical molar amount relative to HF (1/4 molar times). However, by using SiO₂ in an amount larger or smaller than the theoretical molar
10 ratio, the concentration of HF and SiO₂ in the sulfuric acid (waste sulfuric acid) to be discharged in step 2 can be controlled. Taking the matter into consideration that the waste sulfuric acid may be used for other purposes, for example, for its reuse in decomposition of phosphate to give phosphoric acid and for
15 its analysis for process control, it is desirable that SiO₂ is reacted with HF in such a controlled condition that HF is slightly excess over SiO₂.

When the amount of SiO₂ approximates the theoretical molar ratio relative to HF from a low molar ratio thereof, a side
20 product (SiF₃)₂O is formed. This is assumed that SiF₄ produced reacts with SiO₂ to generate the side product.



When (SiF₃)₂O remains contained in SiF₄, it may adversely affect properties of semiconductors and optical fibers produced
25 therefrom, and therefore it must be removed from SiF₄.

Accordingly, SiF₄ containing (SiF₃)₂O formed in step 2, is brought back to the first reactor, in which (SiF₃)₂O is reacted with HF in sulfuric acid in the first reactor to give SiF₄ and water, thereby removing (SiF₃)₂O (step 3).



The reaction condition in this step may be the same as

that in step 1. The reaction of $(\text{SiF}_3)_2\text{O}$ with HF may proceed either in a vapor phase or in a solution of sulfuric acid. When the proportion of $(\text{SiF}_3)_2\text{O}$ produced in the process is large, it is desirable that $(\text{SiF}_3)_2\text{O}$ is introduced into the sulfuric acid solution by bubbling so as to increase the contact time between $(\text{SiF}_3)_2\text{O}$ and HF.

Steps 1 to 3 may be effected batchwise, but it is preferable that the steps be performed continuously. The final product SiF_4 is taken out of the vapor phase in the first reactor.

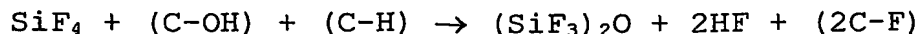
As shown in the above description and Fig. 1, SiF_4 formed in step 1, step 2 and the step 3 each contains HF and H_2O . In general, therefore, SiF_4 taken out of the first reactor is purified in a purification step.

A primary example of purification process is washing with sulfuric acid. By washing with sulfuric acid, HF and H_2O are removed from SiF_4 . The method of washing with sulfuric acid may be conducted, for example, by filling a container with concentrated sulfuric acid and then introducing SiF_4 formed in steps 1 to 3 thereinto. Preferably, the method is more efficiently conducted by introducing sulfuric acid into a column from one direction while introducing SiF_4 from the opposite direction. Also more preferably, the column is charged with a filler for increasing the contact efficiency through it. The higher the sulfuric acid concentration, the more preferable to obtain a higher removal efficiency. Specifically, the sulfuric acid concentration is preferably 90 mass% or higher, more preferably 95 mass% or higher, most preferably 98 mass% or higher. In the absorption column, the sulfuric acid temperature is preferably lower to reduce evaporation of HF and water. However, if the temperature is excessively cooled, the viscosity of the liquid system in the column will increase,

resulting in deterioration of handleability. Accordingly, the absorption column is driven at a temperature within a range of 10 to 50°C. Before use herein, sulfuric acid may be bubbled with N₂ so as to remove CO₂ from it. By using the thus-degassed
5 sulfuric acid, CO₂ in SiF₄ formed in steps 1 to 3 can also be reduced through adsorption by the sulfuric acid.

After having passed through the absorption column, SiF₄ may still contain impurities such as hydrogen chloride, hydrogen sulfide, sulfur dioxide, nitrogen, oxygen, hydrogen, carbon
10 monoxide, carbon dioxide and HF. Of the impurities, those except low-boiling-point components such as nitrogen, oxygen, hydrogen and carbon monoxide may be removed through molecular sieving carbon.

By using the molecular sieving carbon having a pore diameter smaller than the molecular diameter of SiF₄, only
15 impurities such as HCl, H₂S, CO₂ and HF can be adsorbed without adsorbing SiF₄. Preferably, the molecular sieving carbon used herein has a pore diameter of 5 Å or less such as Molsiebon 4A (manufactured by Takeda Pharmaceutical Co., Ltd.). It is
20 preferable that the molecular sieving carbon for use herein be previously baked at a temperature within a range of 100 to 350°C in an inert gas such as N₂ introduced thereto, thereby removing moisture and CO₂ from it. For drying, N₂ having a dew point of -70°C or lower is used, and when the dew point at the
25 baking inlet becomes equal to the dew point at the outlet, the drying may be completed. After thus baked, although moisture is completely removed from the molecular sieving carbon, some hydroxyl group and oxide may still remain on the surface of the adsorbent, and when SiF₄ is introduced, the hydroxyl group
30 and the oxide on the surface of the activated carbon react to generate (SiF₃)₂O and HF.



Accordingly, in a case where an adsorbent after baked is used, prior to the use, the adsorbent surface which may give impurities through reaction with SiF_4 may be allowed to contact and react with SiF_4 , so that formation of the side products $(\text{SiF}_3)_2\text{O}$ and HF may be reduced. Examples of method for contacting the adsorbent include a method of allowing the reaction to proceed while applying SiF_4 to the adsorbent and analyzing impurities at the reactor outlet (e.g., $\text{SiF}_3\text{OSiF}_3$) to confirm the end point, and a method of reacting the two under an accumulated pressure for a predetermined period of time. The contact reaction temperature is not limited as long as the temperature is sufficiently high for adsorption of impurities and the intended contact reaction may proceed without any difficulty, and after the reaction, the adsorbent may complete adsorption of impurities successfully. It is preferable that the reaction be performed under a pressure not higher than the pressure under which SiF_4 is liquefied. From the viewpoint of reducing the amount of SiF_4 to be used for the treatment, it is preferable that the reaction be performed under an atmospheric pressure or a pressure close to it. The purity of SiF_4 to be used is not specifically limited, however, SiF_4 containing a large quantity of impurities is disadvantageous in that the adsorbent may be broken through before the end of the pretreatment, and therefore, the higher the purity of SiF_4 , the more preferable. SiF_4 that contains $(\text{SiF}_3)_2\text{O}$ and HF formed in the pretreatment may be returned back to the reaction step 3 and may be purified.

In a case where SiF_4 contains low-boiling-point components such as N_2 , O_2 , H_2 and CO after removing impurities through adsorption by the molecular sieving carbon, the SiF_4 may be

further purified through a conventional method such as distillation so as to further increase its purity.

Next, the use of the high-purity SiF_4 that is obtained according to the method of the present invention is described.

5 Increasing the transistor integration capacity along with downsizing in semiconductor devices brings about an advantage that a higher density in the device or a higher switching speed of each transistor in the devices can be achieved. However, the propagation delay owing to wiring may wipe out
10 the advantage of transistor speed increment. The generation having a line width of 0.25 μm or more has a serious problem of wiring delay. In order to solve the problem, copper wiring of low resistance is being employed in place of aluminium, and low-dielectric interlayer insulating film is being employed
15 for reducing interconnection capacity. One typical low-dielectric material employed in the generation having a line width of from 0.25 to 0.18 or 0.13 μm is SiOF (fluorine-doped oxide film, having ϵ of 3.5 or so) formed through HDP (high-density) plasma CVD. A process using SiOF as an
20 interlayer insulating film and aluminium alloy as wiring is being employed. It is preferable that SiF_4 for producing such SiOF contain little amount of impurities such as transition metals, e.g., iron, nickel and copper as well as impurities such as phosphorus and boron that may worsen the properties
25 of SiOF . Specifically, it is preferable that the content of transition metal, phosphorus and boron in SiF_4 is 100 ppb or less respectively, more preferably each 50 ppb or less, even more preferably each 10 ppb or less. High-purity SiF_4 of the present invention, satisfying the above requirements, can be
30 used as the doping material for SiOF .

Glass for optical fibers comprises a core and a clad,

in which the core part has a higher refractive index than that of the clad part present around it, so that light may be electrically transmitted smoothly through the center part. In order to increase the refractive index, the core may be doped with a dopant such as Ge, Al or Ti. However, addition of such a dopant may involve a side effect of increasing light scattering in the core, resulting in decrease in the light transmission efficiency of the core. The light transmission efficiency may be increased by using a pure quartz or a quartz doped to a lower degree for the core part and adding fluorine to the clad to make the refractive index lower than that of pure quartz. For fluorine addition to the clad, glass particles (SiO_2) may be heated in an atmosphere of He/SiF_4 . In the SiF_4 atmosphere, it is preferable that the amount of impurities such as transition metals, e.g., iron, nickel and copper as well as phosphorus and boron that may worsen the properties of optical fibers be as small as possible. Specifically, it is preferable that the content of transition metal, phosphorus and boron in SiF_4 is each 100 ppb or less, more preferably each 50 ppb or less, even more preferably each 10 ppb or less. The high-purity SiF_4 of the present invention, satisfying the above requirements, can be used for gas for optical fibers.

Silicon-based solar cells comprises pin-type photoelectromotive force devices. When its I-type semiconductor layer is formed of SiF_4 , the silicon film may contain a small amount of F atoms. In that manner, by including fluorine atoms in the silicon thin film, when the surface of the photoelectromotive force devices receives light irradiation, interactions between heat and fluorine atoms promote the atomic rearrangement in and around the crystal grain boundaries in the devices, thereby alleviating the structural

strain, and in addition, water assumed to penetrate mainly through the grain boundaries from the surfaces of the devices may react with fluorine and the resulting reaction product may bind to unbound valences of silicon atoms or may causes changes in the charge condition of the devices, whereby the optical conversion efficiency of the devices can be self-recovered. It is preferable that the production gas to be used under the condition contain little amount of impurities such as transition metals, e.g., iron, nickel and copper, as well as impurities such as phosphorus and boron that may worsen the properties of the devices. Specifically, it is preferable that the content of transition metal, phosphorus and boron in the production gas be each 100 ppb or less, more preferably each 50 ppb or less, even more preferably each 10 ppb or less. The high-purity SiF_4 of the present invention, satisfying the above requirements, can be used for production of such solar cells.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 shows an outline of the reaction scheme of the invention.

Fig 2. shows an outline of the reaction system usable in the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is specifically described with reference to the following Examples, however, the invention should not be limited thereto.

With reference to Fig. 2, the outline of the production system for use in the present invention is described.

In Fig. 2; 1 and 3 are a sulfuric acid tank and an H_2SiF_6 tank, respectively. Sulfuric acid and H_2SiF_6 are fed to the first reactor (7) via the metering pumps (2, 4), respectively.

In continuous operation, sulfuric acid is fed into the system via the sulfuric acid washing column (5) where a product gas is washed, and the sulfuric acid also functions to purify the product gas. The first reactor (7) is kept at a predetermined temperature by using a heating means (8) such as oil bath. The solutions fed into the first reactor (7) are uniformly mixed by the stirrer motor (6).

In the first reactor, H_2SiF_6 is decomposed into SiF_4 and HF (step 1). Most of SiF_4 gas appears in the vapor phase, and this is taken out via the sulfuric acid washing column (5) into which sulfuric acid is continuously fed. The vapor phase in the first reactor (7) can be sampled out via the sampling valve (11) and analyzed; and the SiF_4 gas having passed through the sulfuric acid washing column (5) can be sampled out via the sampling valve (23) and analyzed.

SiO_2 dispersed in sulfuric acid is fed into the second reactor (17), from the tank (15) via the valve (16). On the other hand, at the time when the solution in the first reactor (7) has reached a predetermined level, the sulfuric acid solution (containing a large amount of side product, HF) in the first reactor (7) is fed to the second reactor (17) via the stop valve (12). The second reactor (17) is kept at a predetermined temperature using a heating means (18) such as oil bath. The solutions fed into the second reactor (17) are uniformly mixed by the stirrer motor (14).

In the second reactor (17), HF formed in step 1 is reacted with SiO_2 to give SiF_4 that contains an impurity, $(\text{SiF}_3)_2\text{O}$, and H_2O (step 2). Most of the SiF_4 gas appears in the vapor phase, and can be sampled out via the sampling valve (10) and analyzed. When the stop valve (9) is opened, the SiF_4 gas can be introduced into the first reactor (7), to react the impurity $(\text{SiF}_3)_2\text{O}$ with

the side product HF formed in step 1 to give SiF_4 (step 3). The sulfuric acid concentration in the second reactor (17) may be controlled by further adding sulfuric acid thereto from the sulfuric acid tank (20). Such a further supply of sulfuric acid can be made, for example, by using metering pump (19). The sulfuric acid may be taken out of the second reactor (17) and introduced into the waste sulfuric acid tank (22) via the valve (21). Accordingly, the liquid level in the system can be arbitrarily controlled .

The mixture of the SiF_4 gas which has been formed in step 1 in the first reactor and the SiF_4 gas which has been formed in step 2 in the second reactor and then purified in step 3 in the first reactor is introduced into the adsorbent (30) that has been previously baked, by opening the stop valve (24) after the reaction in each reactor has reached its steady condition, and the mixture is thereby purified through adsorption with the adsorbent (30) which has been subjected to baking treatment with heating means (31). Generally, baking is performed while introducing N_2 gas from a N_2 source via flow meter (25) and valve (27). Baking may be performed while introducing SiF_4 gas from a SiF_4 source via flow meter (26) and valve (28). The purified outlet gas from the adsorption cylinder (29) may also be sampled via the sampling valve (32) and analyzed. The thus purified gas is taken out of the system via stop valve (33).

Concrete data of the experiment carried out according to the operation mentioned above are shown below. In the following Examples, the dimension of the units that constitute the system is described, however, the present invention can be carried out using units at arbitrary scales, and the reactors and other units may comprise any materials so far as they are resistant to the reaction condition and do not interfere with

the reaction.

Examples 1 to 8:

500 ml of sulfuric acid solution having a concentration
5 previously controlled was fed into the first reactor (7)
(cylindrical reactor made of polytetrafluoroethylene, $\phi 100 \times$
260 length, about 2 liters). The sulfuric acid solution was
heated to the temperature as shown in Table 1, and aqueous 20 %
 H_2SiF_6 solution and 98 % H_2SO_4 were added thereto such that the
10 concentration of the sulfuric acid solution in the reactor could
be kept constant. The sulfuric acid was discharged through
the valve (12) such that the amount of reaction solution in
the reactor could be kept constant. After the reaction reached
its steady condition, the product gas sampled out via the valve
15 (11) was analyzed through FT-IR, and the sulfuric acid solution
sampled out via the valve (13) was analyzed through ion
chromatography. The results are shown in Table 1.

Table 1

Example	Condition for Experiment			Impurity Concentration in SiF ₄				Liquid Composition	
	Supply of 20 % H ₂ SiF ₆ (g/min)	Supply of 98 % H ₂ SO ₄ (g/min)	Reaction Temperature (°C)	HF (vol. %)	HCl (vol. %)	CO ₂ (vol. %)	CO (vol. %)	H ₂ SO ₄ (mass %)	HF (mass %)
1	4.0	24	80	3.5	2.8	0.05	0.09	85	0.8
2	4.0	24	100	5.8	2.9	0.15	0.07	85	0.8
3	4.0	24	120	10.8	2.8	0.17	0.06	85	0.7
4	4.0	16	80	2.8	2.6	0.04	0.11	80	1.1
5	4.0	16	100	5.6	2.7	0.09	0.09	80	1.1
6	4.0	10	80	2.2	2.8	0.05	0.03	73	1.6

Examples 7 to 10:

The H_2SO_4 solution in Example 1 or 4 was constantly supplied into the second reactor (17) ($\phi 100 \times 260$ length, about 2 liters) via the valve (12). A dispersion of SiO_2 in H_2SO_4 was fed into the reactor under an increased pressure with nitrogen, via the metering valve (16) at a constant flow rate relative to the amount of HF in the H_2SO_4 solution fed into the reactor. The temperature of the reaction solution was controlled by the oil bath, and sulfuric acid was constantly discharged out via the valve (21) so that the reaction solution level in the reactor could be kept constant. After the reaction reached its steady condition, the product gas was sampled out via the valve (10) and analyzed through FT-IR. The results are shown in Table 2.

Table 2

Example	Condition for Experiment						Impurity Concentration in SiF ₄		
	HF-containing H ₂ SO ₄ used	HF-containing H ₂ SO ₄ (g/min)	SiO ₂ dispersion in H ₂ SO ₄		Reaction Temperature (°C)		HF (vol.%)	CO ₂ (vol.%)	(SiF ₃) ₂ O (vol.%)
			Supply (g/min)	SiO ₂ Concentration (mass%)					
7	Example 4	17.5	1.8	4.0	80		0.5	0.001	ND*
8	Example 4	17.5	2.88	4.0	80		0.02	0.002	0.1
9	Example 4	17.5	3.5	4.0	80		ND	0.001	1.7
10	Example 1	27.2	4	4.0	80		ND	0.001	1.9

*ND: not detected (less than detection limit)

Examples 11, 12:

The SiF_4 gas obtained in Example 9 was fed into the first reactor (7) via the valve (9), in which the reaction was continuing under the same condition as in Example 4. The product gas was sampled out via the valve (11), and analyzed through FT-IR. In addition, the product gas was led through the sulfuric acid washing column (5), and then sampled out via the valve (23) and analyzed through FT-IR. As sulfuric acid washing column (5), a 50 cm long 1/2-inch tube made of polytetrafluoroethylene, which was filled with a filler of polytetrafluoroethylene (120 ml), was used. The results are shown in Table 3.

Table 3

	Impurity Concentration in SiF_4						Amount of SiF_4 formed (Nml/min)
	Sample Valve	HF (vol.%)	HCl (vol.%)	CO_2 (vol.%)	CO (vol.%)	$(\text{SiF}_3)_2\text{O}$ (vol.%)	
Example 11	11	1.9	1.7	0.11	0.04	ND*	184
Example 12	23	0.01	1.8	0.11	0.04	ND*	184

* ND: not detected (less than detection limit)

Examples 13, 14:

The gas in Example 12 was introduced into the adsorption cylinder (29). The adsorption properties were compared between a case using an adsorbent baked with N_2 alone and a case using an adsorbent baked with N_2 and further pretreated with SiF_4 .

As the adsorption cylinder, a 3/4-inch SUS tube was used, and was filled with 100 ml of an adsorbent, Molsiebon 4A (manufactured by Takeda Pharmaceutical Co., Ltd.). The adsorbent was baked at 300°C with N_2 applied thereto at a rate of 400 ml/min, and the baking was continued until the outlet dew point reached -70°C or lower. After this was cooled to room temperature, and the same gas as that in Example 12 was introduced

thereinto, and the outlet gas was analyzed.

In the other case, where the baked adsorbent was further treated with high-purity SiF_4 , SiF_4 was introduced to the adsorbent at room temperature at a flow rate of 100 ml/min, and the outlet gas was intermittently analyzed through FT-IR. The pretreatment was continued until no hexafluorodisiloxane was detected in the outlet gas. After completion of the pretreatment, the same gas as that in Example 12 was introduced thereto, and the outlet gas was analyzed. The results are shown in Table 4 and Table 5.

10

Table 4

Example 13 (not pretreated with SiF_4)				
	Impurity Concentration in SiF_4			
Time (min)	HF (vol.%)	HCl (vol.%)	CO_2 (vol.%)	$(\text{SiF}_3)_2\text{O}$ (vol.%)
10	0.05	ND*	ND*	0.13
30	0.04	ND*	ND*	0.1
60	0.01	ND*	ND*	0.05

*ND: not detected (less than detection limit)

Table 5

Example 14 (pretreated with SiF ₄)				
	Impurity Concentration in SiF ₄			
Time (min)	HF (vol.%)	HCl (vol.%)	CO ₂ (vol.%)	(SiF ₃) ₂ O (vol.%)
10	ND	ND	ND	ND
30	ND	ND	ND	ND
60	ND	ND	ND	ND

ND: not detected (less than detection limit)

As seen in the above results, SiF₄ gas containing impurities in an amount undetectable through FT-IR could be continuously produced.

INDUSTRIAL APPLICABILITY

As described above, the present invention enables continuous production of SiF₄ gas containing impurities at a concentration reduced to a level as low as undetectable through FT-IR. Accordingly, the present invention enables production of high-purity SiF₄ that has been demanded in the electronic component industry. Moreover, according to the present invention, HF that is discarded as a side product in conventional methods can be utilized in producing SiF₄, and the utilization efficiency of starting materials is high, and discharge of harmful substances can be reduced.